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THE ELECTROLYTIC OXIDATION OF IODINE AND OF IODIC ACID

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THE ELECTROLYTIC OXIDATION OF IODINE AND OF IODIC ACID.¹

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ABSTRACT.

A cell for the electrolytic oxidation of iodine to iodic acid is described. This oxidation was effected by means of a platinum anode in a solution containing hydrochloric acid as the iodine carrier. A similar cell was used to oxidize iodic acid to periodic acid, in the absence of chlorides, using a lead dioxide anode. Both acids may be obtained in crystalline form by evaporation of their respective anode solutions. A commercial grade of iodine may be used as a raw material since pure iodic acid (HIO_3) and pure para-periodic acid (H_5IO_6) may easily be secured from the crude product by recrystallization from concentrated nitric acid.

PART I. THE ELECTROLYTIC OXIDATION OF IODINE.

Several chemical methods for the oxidation of iodine to iodic acid have been proposed. The use of chloric acid for this purpose was first reported by H. Kammerer⁴ and has been further developed by Lamb, Bray and Geldard.⁵ The high cost of iodic acid prepared by this method has discouraged its more general use. Fuming nitric acid was used to oxidize iodine to iodic acid by A. Connell⁶ and A. Duflos⁷ in 1831, and their procedure has been modified by numerous workers since that time. The nitric acid method is both troublesome and dangerous. Other oxidizing agents have been suggested but have found little use.

A. Riche⁸ in 1858 suggested that iodic acid could be prepared by electrolysis of solutions of iodine or hydriodic acid. He electrolyzed these

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⁴ H. Kammerer, *Pogg. Ann.*, **138**, 227, 400 (1871).

⁵ A. B. Lamb, Wm. C. Bray and W. J. Geldard, *J. Am. Chem. Soc.*, **42**, 1636 (1920).

⁶ A. Connell, *New Edin. Phil. Journ.*, **10**, 53, 337; **11**, 72 (1831).

⁷ A. Duflos, *Schweigger's Journ.*, **62**, 496 (1831).

⁸ A. Riche, *Compt. rend.*, **46**, 348 (1858).

materials between platinum electrodes and claimed to have formed iodic acid. Riche's method is not suitable as a method for the preparation of iodic acid (as he claimed), since he provided no means of preventing the reduction of the iodic acid at the cathode.

OXIDATION POTENTIALS.

During a few of the electrolytic oxidations of iodine to iodic acid the anode potentials and the oxidation potentials of the solutions were recorded from time to time. These potentials were measured by comparison with a saturated calomel electrode, using a simple potentiometer set-up. The bright platinum foil, for securing the oxidation potentials, and the capillary tip of the calomel half-cell were located inside the cylindrical anode in order to keep them out of the "IR" field between the anode and cathode.

The curves in Fig. 2 and 3 represent the anode and oxidation potentials during the conversion of iodine to iodic acid. In every case a rise of both the anode and oxidation potentials was observed at the time the iodine color was lost by the anode solution. Up to that time no evolution of gas was noticeable, but coincident with the completion of the iodine oxidation, both chlorine and oxygen began to evolve.

EXPERIMENTAL.

The design of the cell adopted for the electrolytic oxidation of iodine and of iodic acid is shown in Fig. 1. The porous earthen cup⁹ formed the anode compartment and was surrounded by a two liter beaker which served as the cathode chamber. A copper tube plated with silver and then with gold was coiled around the porous cup and served as both the cathode and cooling coil. A gold surface was desirable because of its lesser tendency to catalyze the cathodic reduction of nitric acid to ammonia. By circulating tap water through this coil the temperature of the entire cell could be held well below room temperature, even with 15 to 20 amperes passing through the system. The anode for the oxidation of iodine to iodic acid consisted of a smooth platinum cylinder of about 90 sq. cm. outside area.

An experimental cell was also constructed of a small battery jar with a compressed asbestos diaphragm cemented vertically through the middle, dividing the space into separate anode and cathode compartments. This cell was used to test the utility of asbestos membranes as substitutes for porous earthen cups. The electrical conductivity through

⁹ Inside diameter 7 cm., height 19 cm.; from The Coors Porcelain Company.

the asbestos diaphragm was as good as that of the earthen cup, though electro-endosmosis and diffusion were slightly more pronounced with the former. Since the cylindrical type of cell was much more convenient and more easily cooled, the asbestos membrane was used only to demonstrate its possibilities. If available in cylindrical form, asbestos membranes should function quite satisfactorily.

The slight solubility of iodine in water necessitated the use of a more effective solvent. Although either iodic or periodic acids (depending on the type of anode used) could be produced by the electrolysis of an iodine suspension without the use of an iodine carrier, the process was

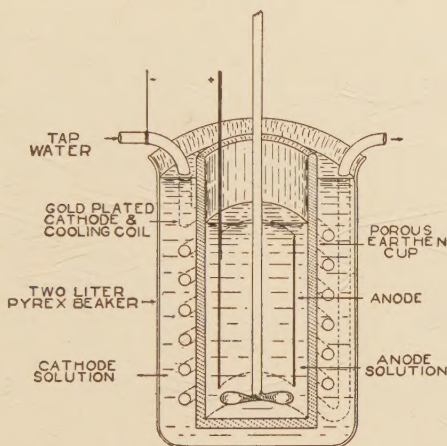
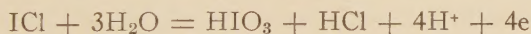


FIG. 1. Cell for Electrolytic Oxidation of Iodine and of Iodic Acid.

too slow for practical application. The addition of a small amount of iodine monochloride served to speed up the rate of solution of iodine and the oxidation reaction functioned efficiently as long as free iodine remained in suspension, and provided excessive current densities were not used. If the oxidation reaction is assumed to be



and the reaction for the reformation of the iodine chloride



it appears that an equivalent amount of hydrochloric acid might be used as an iodine carrier in place of the iodine chloride. Dilute hydrochloric acid solutions were found to be entirely satisfactory and were used in obtaining the data reported in this paper.

During electrolysis the process of electrical transfer carried the anions of the catholyte through the porous cup into the anode solution. Hence, in order to recover the products of the oxidation by evaporation of the anode solutions, the catholyte must be non-reducing in character and easily volatile. Hydrochloric acid could not be used because of its reducing action, and perchloric, sulfuric and phosphoric acids are not easily volatile. Nitric acid satisfied these requirements although it was subject to cathodic reduction and, if electrolysis was continued without changing the cathode solution, was finally converted into ammonia. By

TABLE I.

*Electrolytic Oxidation of Iodine in HCl Solutions.*Volume of anode solutions, 500 cc. Cathode solutions, 2N HNO₃.

Exp. No.	Anode Area sq. cm.	Current amp.	Anode Current Density amp./sq. cm.	Amp.-hr. used for Oxidation	Conc. of HCl in Anode Sol'n. N	Iodine used grams	Iodic Acid recovered grams	Iodic Acid Yield per cent	Current Efficiency per cent
96	85	6.0-10.5	0.07-0.12	292	0.8	295	375	92.0	97.7
97	85	8.0-11.0	0.09-0.13	108	0.4	103	130	91.0	91.5
98	65	8.0-11.0	0.12-0.17	103	0.2*	<100	122	**	**
99	65	12.0-15.0	0.19-0.23	**	0.3*	100	125	90.3	**
100	92	11.5-16.8	0.13-0.18	113(?)	0.4	100	126	91.0	84.7(?)
101	92	5.0	0.06	104	0.2	100	126	91.0	92.5

* Rate of oxidation more rapid than rate of solution of iodine. (Anode solution lost its color of iodine while solid iodine still remained.)

** Not determined.

changing the cathode solution before it had become alkaline, satisfactory operation was maintained.

Attempts were made to use hydrofluoric acid both as the cathode solution and as iodine carrier in the anode solution, but the solubility of iodine in such a solution was too low. No material was found which would serve this dual role.

The phenomenon of electro-endosmosis was very noticeable in the smaller cells used in preliminary work, the anode solution being carried outward through the porous cup into the cathode solution. This loss was practically eliminated through the use of a cell sufficiently tall to permit the maintenance of the cathode solution level about 5 cm. above the level of the anode solution. This arrangement also prevented losses of the anode solution by simple diffusion through the porous cup.

Several materials were tried as anodes in an attempt to find a substitute for platinum. Graphite, both artificial and natural, was found

to disintegrate rapidly under the influence of anodic reactions in nitric and hydrochloric acid solutions. Carborundum, in the form of "Globar" furnace elements, failed to withstand the anodic corrosion due to attack on the binder. The carborundum itself was wholly inert and possibly a pure carborundum rod would have functioned satisfactorily. Such a rod, however, was not available at the time of these experiments.

The cathode compartment of the cell was filled with 2*N* nitric acid and the anode with dilute hydrochloric acid. From 25 to 300 grams of iodine was pulverized and added to the anode solution. A purified grade of iodine, though usually used, was not necessary since the final prod-

TABLE II.

Decomposition of HIO₃ by HCl.

Volume of anode solution, 100 cc. Area of anode, 50 sq. cm. Current, 5.0 amp. Anode current density, 0.1 amp./sq. cm. Concentration of HCl in anode solution, 1*N*. Cathode solution, 2*N* HNO₃.

Exp. No.	Amp./hr. for Oxidation	Iodine used grams	Iodic Acid recovered grams	Iodic Acid Yield per cent	Iodine in Distillate grams	Iodine in Distillate per cent	Iodine in Cathode Solution grams	Iodine in Cathode Solution per cent	Total Iodine Accounted for per cent
92	27	25	31.0	89.4	1.85	7.4	0.6	2.3	99.1
93	27	25	29.5	85.1	1.78	7.1	1.0	4.1	96.3
91	55	54	64.5	86.3	1.80	3.4	*	*	(89.6)

* Not determined.

ucts are easily purified by crystallization. After stirring the anode solution for a few minutes, electrolysis was started and continued until all of the iodine had been oxidized.

Table I illustrates the electrolytic oxidation of iodine to iodic acid when using hydrochloric acid as the iodine carrier. When passing a current of 10 amperes or more through the cell, hydrochloric acid concentrations less than 0.3*N* (No. 98 and 99) were not high enough to insure continuous operation of the cell, but when the current was sufficiently reduced (No. 101) these concentrations of chloride were found to dissolve iodine as rapidly as oxidation took place. The rate of stirring was also found to influence the continuity of the process.

In each experiment in Table I, electrolysis was discontinued as soon as the iodine color in the anode solution was lost and chlorine was evolved. The anode solution was siphoned into a casserole and evaporated on a hot plate. During evaporation of these solutions, the liquid became orange colored and orange and violet vapors were evolved. In

order to collect and analyze these vapors, a Pyrex distilling apparatus was constructed so that the anode solutions could be drawn from the cell and evaporated by distillation at either reduced or atmospheric pressure.

The cathode solutions, including the iodine materials from the pores of the porous cup, were likewise examined for their iodine content. The distillates from the anode solution and the cathode solution were completely reduced with sulfite and the iodide titrated potentiometrically with standard silver nitrate solution, using a silver indicator electrode. The data so obtained are listed in Table II, which indicates that the

TABLE III.

Effect of HNO_3 on the Reduction of HIO_3 by HCl .

Volume of anode solutions, 500 cc. Area of anode, 92 sq. cm. Current, 10 amp. Anode current density, 0.11 amp./sq. cm. Cathode solutions, 2N HNO_3 .

Exp. No.	Amp./hr. used for Oxidation	Concentration of HCl in Anode Solution N	HNO_3 added to HIO_3 Solution during evaporation cc. conc.	Iodine used grams	Iodic Acid recovered grams	Iodic Acid Yield per cent	Oxidation Current Efficiency per cent	Electrical Energy consumed watt-hr.
102	106	0.4	None	100	127.5	92.0	91.6	450
103	105	0.4	100	100	129.0	93.2	93.4	440
104	104	1.6	None	100	108.5	78.4	79.5	415
105	104	1.6	100	100	112.0	81.0	82.0	410

amount of iodic acid lost through reduction by hydrochloric acid was determined by the amount of chloride present.

Table III shows the results of an attempt to remove the chloride by the addition of nitric acid to the solution before evaporation. Only a slight improvement in the yield of iodate was noted. Table IV presents data showing that a much more effective method was to evolve the chlorine, as such, by continuation of electrolysis, after the iodine was all oxidized, until no more chlorine was liberated. The yields of iodic acid listed in Table IV are typical of this electrolytic oxidation process. During the latter stages of the evaporation of the iodic acid solutions, fumes of perchloric acid were noted, indicating that a part of the chlorine was oxidized to perchloric acid instead of being liberated as free chlorine. Continued heating at 100° to 120° C. effected the removal of this acid in from 10 to 24 hours. The presence of nitric acid in these solutions during evaporation greatly facilitated the crystallization of the iodic acid.

In this work the iodic acid solutions were evaporated to dryness merely for the purpose of determining the yields of iodic acid. In practice, if periodic acid is wanted, the platinum anode need only be replaced by a lead dioxide anode and the oxidation continued to periodic acid. In one experiment this was done as follows: 250 grams of iodine was added to about 600 cc. of a 0.7*N* hydrochloric acid solution in the anode compartment of the cell. The iodine was oxidized using a bright platinum

TABLE IV.

Removal of Chlorine by Electrolysis.

Volume of anode solution, 500 cc. Area of anode, 92 sq. cm. Current, 10 amp. Anode current density, 0.11 amp./sq. cm. Cathode solutions, 2*N* HNO₃.

Exp. No.	Over-time Elec- trolysis hr.	Amp./hr used for Oxida- tion	Concen- tration of HCl in Anode Solution <i>N</i>	Iodine used grams	Iodic Acid recovered grams	Iodic Acid Yield per cent	Current Efficiency of Iodine Oxidation per cent	Total Current Efficiency per cent	Electrical Energy consumed watt-hr.
108	1.25	101	0.4	100	129	93.2	93.6	84.0	495
110	1.5	104	0.4	100	132	95.4	96.5	84.4	535
111	1.5	101	0.4	100	130	93.8	99.0	85.7	495
120	1.5	104	0.4	100	132	95.4	96.5	85.0	510
109	2.0	104	0.4	100	131	94.6	94.1	79.0	515
121	2.0	103	0.4	100	131	94.6	96.8	81.8	550
112	2.0	104	0.4	100	132	95.4	96.6	81.7	505
114	2.0	105	0.4	100	133	96.0	96.2	81.5	545
115	2.0	104	0.4	100	134	96.7	98.0	82.3	545
116	2.0	105	0.4	100	132	95.4	95.5	80.0	565
106	2.5	101	0.4	100	130	94.0	98.0	78.6	555
107	3.0	105	0.4	100	131	94.6	95.0	74.7	590
117	2.0	210	0.6	200	263	95.0	95.3	87.8	1,025
118	2.0	208	0.6	200	265	95.7	97.0	88.5	960
119	2.0	207	0.6	200	265	95.7	97.5	88.5	935
122	2.0	210	0.6	200	265	95.7	96.1	88.2	940
123	5.5	209	0.6	200	264	95.4	96.6	76.0	1,035

anode of 92 sq. cm. area with a current of about 15 amp. The oxidation of the iodine to iodic acid and the evolution of the chlorine were completed in about 20 hours.

A lead dioxide anode of about 85 sq. cm. area was then substituted for the platinum anode and the iodic acid oxidized to periodic acid. After 24 hours at about 13 amperes, the anode solution showed a negative test for iodate. The solution was then filtered and evaporated by vacuum distillation. There was recovered 430 grams of periodic acid, representing a yield of 96.0 per cent of the theoretical based on the iodine used.

PART II. THE ELECTROLYTIC OXIDATION OF IODIC ACID.

The use of periodates as analytical reagents has been greatly retarded due to the difficulty in obtaining them. Until recently the chemical methods for the preparation of periodates were both long and troublesome, especially that of the free acid. In certain analyses periodic acid has the distinct advantage over its salts in that no metal ions are introduced into the solutions, as in the separation of potassium from sodium.¹⁰

Müller^{11, 12} showed that iodates could be oxidized electrolytically to periodates by use of smooth platinum anodes in alkaline solutions, but not in neutral or acid solutions. Müller and Friedberger¹³ were able to show that iodic acid itself could be oxidized electrolytically to periodic acid, though their procedure was not suitable as a method of preparation. Oxidation of the iodic acid was effected by a lead anode coated with lead dioxide, using a porous earthen cup to separate the anode and cathode solutions. Their use of this lead-lead dioxide anode was possible because of the sulfuric acid cathode solution employed, but efficient recovery of the periodic acid in a solid form was impossible because of

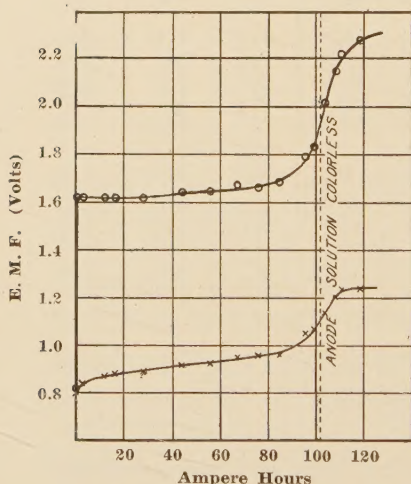


FIG. 2. Electrolysis No. 120. Anode Solution, 100 g. Iodine in 500 cc. 0.4 *N* HCl Solution; Anode, Bright Platinum; Anode Area, 92 sq. cm.; o, Anode Potentials; x, Oxidation Potentials.

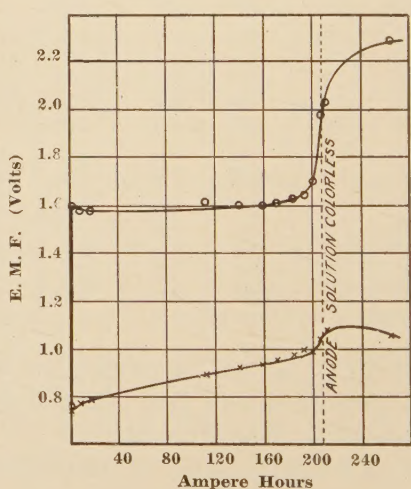


FIG. 3. Electrolysis No. 123. Anode Solution, 200 g. Iodine in 500 cc. 0.6 *N* HCl Solution; Anode, Bright Platinum; Anode Area, 92 sq. cm.; o, Anode Potentials; x, Oxidation Potentials.

¹⁰ Unpublished work by one of the authors (H. H. W.).

¹¹ E. Müller, *Z. Elektrochem.*, **5**, 469 (1899).

¹² E. Müller, *ibid.*, **7**, 509 (1901).

¹³ E. Müller and A. Friedberger, *Ber.*, **35**, 2652 (1902).

the difficulty of removing the sulfuric acid which accumulated in the anode solution.

Müller¹⁴ studied also the influence of oxygen overvoltage and the catalytic action of lead dioxide and concluded that, (a) since the oxygen overvoltage on platinum was higher in alkaline solution than in neutral or acid solution, periodates could be formed at platinum anodes in alkaline solution, but that (b) the production of periodic acid at a lead dioxide anode in acid solution must be attributed to the catalytic influence of the lead dioxide. (The oxygen overvoltage on lead dioxide is actually less than that on smooth platinum.¹⁵)

OXIDATION POTENTIALS.

In Fig. 5 potential curves (similar to those for the oxidation of iodine in Fig. 2 and 3) are shown for the oxidation of iodic acid to periodic acid by use of a lead dioxide anode. The curves of Fig. 4 represent the potentials recorded when iodic acid was electrolyzed with a bright platinum anode instead of a lead dioxide anode, all other conditions being the same. (See page 250.)

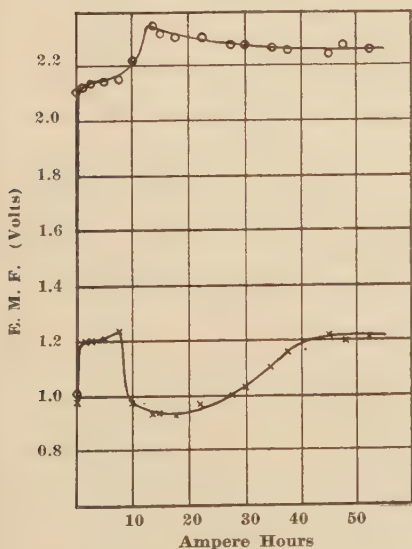


FIG. 4. Electrolysis No. 229. Anode Solution, 50 g. HIO_3 in 100 cc. Water; Anode, Bright Platinum; Anode Area, 47 sq. cm. Current, 5 amp.; o, Anode Potentials; x, Oxidation Potentials.

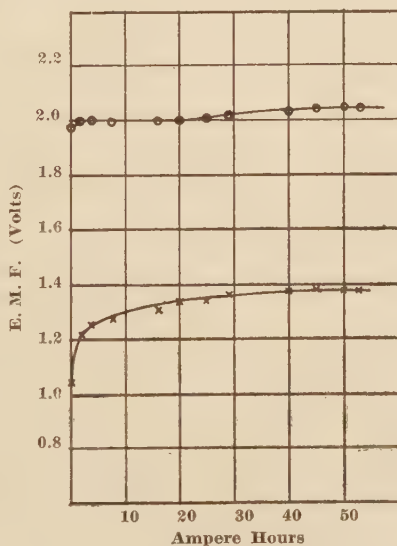


FIG. 5. Electrolysis No. 232. Anode Solution, 50 g. HIO_3 in 100 cc. Water; Anode, Lead Dioxide; Anode Area, 47 sq. cm.; Current, 5 amp.; o, Anode Potentials; x, Oxidation Potentials.

¹⁴ E. Müller, *Z. Elektrochem.*, **10**, 49 (1904).

¹⁵ C. L. Mantell, "Industrial Electrochemistry," p. 54, McGraw-Hill (1931).

No entirely satisfactory explanation of the shapes of the early portions of these curves (Fig. 4) has yet been offered, but the final equilibrium potentials (after 40 amp.-hr.) were approximately the same as the corresponding potentials of the curves of Fig. 2 and 3. However, the final potential assumed by the lead dioxide anode (Fig. 5) was about 0.2 volt lower than that of the platinum anodes. Since a vigorous evolution of oxygen took place throughout the entire period of electrolysis in both cases, this difference in anode potentials may be explained by recalling that the oxygen overvoltage on lead dioxide is about 0.2 volt lower than that on platinum.¹⁵ The oxidation potential of the solution electrolyzed with the lead dioxide anode was about 0.2 volt higher than the oxidation potentials of the solutions in which platinum anodes were used. The conversion of the iodic acid to periodic acid would be expected to cause this increase in the oxidation potential.

Little periodate was produced when using platinum anodes even though operated at higher potentials than the lead dioxide anodes, which easily accomplished the oxidation of iodic acid to periodic acid. These observations are in agreement with Müller's claim that lead dioxide anodes were capable of producing periodates in acid solution because of a catalytic rather than an overvoltage effect.¹⁴

The peculiar shapes of the curves (Fig. 4) for the electrolysis of iodic acid solutions with platinum anodes suggested the possibility that periodic acid may have been formed during the early part of the electrolysis and had subsequently decomposed. A direct qualitative test for periodate capable of detecting 0.1 mg. in the presence of 50 mg. of iodate has been described by Thompson.¹⁶ Even larger amounts of iodate may be removed as barium iodate, permitting a still more delicate test for periodate.

Experiment No. 229 (Fig. 4) was duplicated in order to test the anode solution for periodate at intervals during the electrolysis. Since the anode solution contained 0.5 gram of iodic acid per cc., the test was performed as follows: a 1 cc. sample was diluted to 50 cc. with water, acidified with 2 cc. of perchloric acid (70 per cent) and heated nearly to boiling before adding 2 grams of barium nitrate. When the latter had completely dissolved, the solution was chilled, filtered and 5 cc. of a solution of bismuth nitrate added. This solution contained 35 grams of bismuth nitrate and 150 cc. of 2*N* perchloric acid per liter.

¹⁶ J. J. Thompson, Thesis, "The Determination of Lead, Manganese and Mercury by Means of Periodate." University of Michigan, June, 1931.

The sample withdrawn from the anode solution after 15 minutes of electrolysis gave a turbidity of bismuth periodate that corresponded to about 1 mg. of periodic acid per cc. Samples taken after longer periods of electrolysis yielded such heavy precipitates of bismuth periodate that they could not be compared with standard periodate solutions. By using 1 drop samples of the anode solution, the periodate could be estimated directly without first removing the iodate. After 5 hours electrolysis, the amount of periodate appeared to remain constant at about 4 mg. per cc., or a total of about 0.4 gram in the entire solution.

This series of tests was made using 1 drop samples in 50 cc. of water, 5 cc. of perchloric acid (70 per cent) and 5 cc. of the bismuth nitrate solution described above. The periodate content was estimated as before by comparison of the turbidities of the samples with those of standard solutions of periodate. In all cases enough perchloric acid was present to prevent any precipitation of bismuth iodate, as determined by blanks.

The amount of periodic acid formed by a platinum anode was thus shown to increase until an equilibrium was established between the rates of formation and decomposition. It is probable that the platinum itself acts as a catalyst for the decomposition of periodate, since it is known that a small amount of platinum black, when added to a solution of periodic acid, causes a rapid evolution of oxygen. Lead dioxide, on the other hand, is capable of slowly oxidizing iodic acid to periodic acid.¹⁴

EXPERIMENTAL.

The oxidation of iodic acid to periodic acid was accomplished in a cell similar to that used for the oxidation of iodine to iodic acid (Fig. 1), except that a lead dioxide anode was substituted for the platinum anode. The cathode compartment of the cell was first filled with 2*N* nitric acid, after which the iodic acid, dissolved in water, was placed in the porous cup. The cathode solution level was kept higher than the anode solution in order to prevent loss of the anode solution through the porous cup by diffusion. Thorough mixing of the anode solution was provided by a motor driven stirrer.

The anodes for the oxidation of iodic acid to periodic acid were made by plating lead dioxide on platinum gauze cylinders. Lead dioxide deposits of approximately equal durability were secured from acid and neutral plating baths. The acid bath consisted of a 25 to 50 per cent nitric acid solution saturated with lead nitrate and containing 1 to 2 cc. of sulfuric acid and about 5 drops per liter of a syrupy sodium silicate

solution. The strong nitric acid solution prevented cathodic deposition of lead, the sulfuric acid improved the adhesion of the deposit and the silicate gave a smooth or velvety surface. The sodium silicate was diluted with water before being added to the strongly acid solution.

After long standing, silicic acid separated from the solution and interfered with the deposition of lead dioxide, hence it is recommended that

TABLE V.

Electrolytic Oxidation of Iodic Acid to Periodic Acid.

Volume of anode solutions (except last three), 100 cc. Volume of anode solutions No. 234, 235 and 237, 400 cc. Cathode solutions, 2N HNO₃.

Exp. No.	Current amperes	Anode Current Density amp./-sq. cm.	Iodic Acid used grams	Yield of Crude H ₅ IO ₆ grams	Yield of Crude H ₅ IO ₆ per cent	Total amp.-hr.	Total Current Efficiency per cent	Electrical Energy consumed watt-hr.
Area of Outer Surface of Cylindrical Lead Dioxide Anode—21.5 sq. cm.								
216	5.0	0.23	50	62.5	96.9	53	27	...
217	4.0	0.19	50	63.0	97.7	36	43	...
219	3.0	0.14	50	62.0	96.1	36	43	...
220	5.0	0.23	50	62.0	96.1	45	34	...
221	6.0	0.28	50	64.0	99.2	51	30	...
222	5.0	0.23	50	62.0	96.1	53	29	...
223	5.0	0.23	50	59.0	91.5	45	34	170
229	5.0	0.23	50	60.0	93.0	40	38	150
238	5.0	0.23	50	62.5	96.9	43	36	190
Area of Outer Surface of Cylindrical Lead Dioxide Anode—47 sq. cm.								
226	5.0	0.11	50	59.0	92.3	40	38	150
228	5.0	0.11	50	60.0	93.0	71	22	270
230	5.0	0.11	50	60.5	93.8	55	28	206
232	5.0	0.11	50	62.0	96.1	53	29	203
239*	5.0	0.11	50	61.0	94.6	63	24	280
234	5.0	0.11	100	129.5**	100.0**	88	35	368
235	6.0	0.13	200	264.5**	102.0**	141	43	635
237	6.0	0.13	300	387.5**	100.0**	191	48	895

* Platinum gauze of the anode exposed.

** High yields listed are due to incomplete drying of large amounts of H₅IO₆.

the solution be freshly prepared when needed. A current density of 0.025 to 0.050 amp. per sq. cm. was most satisfactory. The neutral bath was made up according to the directions of Ferchland,¹⁷ using a 25 per cent lead nitrate solution which was maintained approximately neutral through addition of lead oxide. A current density of 0.025 to 0.050 amp. per sq. cm. was used.

When graphite and carborundum ("Globar" elements) were tried as supports for lead dioxide coatings, it was found that the lead dioxide

¹⁷ P. Ferchland, Z. Elektrochem., 9, 670 (1903).

was too porous to protect the base material from attack by the solution, as described in Part I. Solid lead dioxide electrodes were constructed by plating on a carbon rod and later removing the carbon, but due to the high resistance of the lead dioxide, no satisfactory connection could be secured.

While attempting the direct oxidation of iodine to periodic acid, using lead dioxide anodes and iodine chloride or hydrochloric acid as the iodine carrier, the lead dioxide electrodes were very severely attacked. Such disintegration of the anodes did not occur in the absence of chlorides, hence the attempt to oxidize iodine directly to periodic acid was abandoned in favor of the two stage process: (a) the oxidation of iodine to iodic acid by means of a platinum anode in a chloride solution,

TABLE VI.

Relation of Current Density to Current Efficiency.

Outer area of cylindrical lead dioxide anode, 21.5 sq. cm. Volume of anode solution, 100 cc. Iodic acid used, 50 grams.

Exp. No.	Current amperes	Anode Current Density amp./sq. cm.	Yield of Crude H_5IO_6 grams	Yield of Crude H_5IO_6 per cent	Amp.-hr. used for Oxidation	Current Efficiency per cent
219	3.0	0.14	62.0	96.1	33	47
217	4.0	0.19	63.0	97.7	32	48
220	5.0	0.23	62.0	96.1	35	44
221	6.0	0.28	64.0	99.2	40	38

and (b) after removal of chlorides, the oxidation of the iodic acid to periodic acid by use of a lead dioxide anode. Table V lists the results of a series of oxidations of iodic acid.

The data of Table VI show that low current densities favored higher current efficiencies. However, the use of low currents prolonged the oxidations unduly and thereby increased the losses of iodine by diffusion through the porous cup. Hence it is desirable to use: (a) a large anode surface and (b) a high current, resulting in (c) a shorter time of electrolysis. When using an anode surface of 85 sq. cm. and a current of 12 to 15 amperes, it was possible to oxidize 300 grams of iodic acid to periodic acid in about 24 hours.

Completion of the oxidation of iodic acid was determined by testing a 2 or 3 drop sample of the solution with silver nitrate in a dilute sulfuric acid solution, warmed to 40° to 50° C. The presence of iodate was indicated by a white precipitate of silver iodate (the yellow silver periodate being soluble in dilute acid). When completely oxidized the

periodic acid solution was siphoned off and evaporated to dryness to determine the yield.

Originally the solutions were evaporated in conical flasks in a drying oven at 70° to 85° C. Purified air was passed into the flasks to sweep out the water and nitric acid vapors. Very little decomposition of the periodic acid could be noted until after the acid had begun to crystallize, after which decomposition was more serious and iodic acid was formed as a yellow powder. By conducting the evaporation of the periodic acid solutions in a vacuum distilling apparatus at 40° to 60° C., practically

TABLE VII.
Recrystallization of Periodic Acid.

First, second and third crops were twice recrystallized from HNO_3 . Reoxidized residues were weighed without being recrystallized.

Sample No.	Impure H_2IO_6 grams	First Crop grams	Second Crop grams	Third Crop grams	Total Pure H_2IO_6 recovered grams	Total Pure H_2IO_6 recovered per cent	Reoxidized Residues grams	Total Recovery grams	Total Recovery per cent	
1	229	129	167	104	910	83.2	134	1,044	95.5	
2	234	268								
3	317									
4	313	190	52							
5	490	273	154	104	273	55.7	396	1,606	99.5	
6	780	552			937					83.5
7	343	231								
Totals	2,706	1,643	373	104	2,120	78.3	530	2,650	97.9	

all decomposition was avoided. In addition, the vacuum evaporation could be completed in a small fraction of the time formerly required.

The evaporation of the periodic acid solutions must not be carried to dryness since overheating is unavoidable in such a procedure. It is preferable to add nitric acid to the periodic acid solution and evaporate until periodic acid begins to crystallize out. If the solution is then allowed to cool, most of the periodic acid separates.

After pouring off the remaining liquid, the crystals of para-periodic acid were dissolved in hot, concentrated nitric acid (free from nitrous acid), filtered through glass or porcelain filters and recrystallized by cooling. Recrystallization of periodic acid from aqueous solution was not considered feasible because of the high solubility. Periodic acid exhibited a pronounced tendency to form supersaturated solutions, even

in concentrated nitric acid, and was therefore usually permitted to crystallize overnight. The nitric acid was then poured off and the crystals drained centrifugally. This crop of crystals was again dissolved in nitric acid and recrystallized.

Except in case of the residues, two recrystallizations yielded a product that gave no test for iodate. Only a trace of iodate was present after one recrystallization. After centrifuging, the crystals were placed over solid potassium hydroxide in a vacuum desiccator to remove the last traces of nitric acid. The drying process was greatly hastened by warming the desiccator to about 40° C. Table VII indicates that practically all of the periodic acid may be recovered from the recrystallizing process.

The original aqueous mother liquors were collected, together with the nitric acid used for recrystallization, and subjected to vacuum distillation in order to recover the periodic acid residues. Three crystallizations from nitric acid were sometimes required in order to free this material from iodic acid. The final residues were returned to the oxidation cell for reoxidation.

While oxidizing a sample of iodic acid, a defective lead dioxide coating on the outer surface of the anode became loosened and fell off, thereby exposing a greater surface area of platinum gauze than there remained of the lead dioxide. In spite of this circumstance the anode continued to function, as was clearly shown by refilling the cell with a new sample of iodic acid and oxidizing it with the same electrode. The oxidation was completed in a slightly longer time than usually required when using a normally coated lead dioxide anode. Apparently the exposed platinum did not greatly reduce the efficiency of the remaining lead dioxide surface, at which, through its catalytic effect and lower oxygen overvoltage, the anode reactions took place in preference to the platinum surface.

The electrochemical oxidation of iodine either to iodic acid or to periodic acid is thus shown to be entirely feasible and in comparison to the cost of the iodine, the expense of the process is reasonable.

